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Wastes from Manufacture of Dyes and Pigments. Volume 7 Xanthene Dyes and Pigments

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WASTES FROM MANUFACTURE OF DYES AND PIGMENTS: VOLUME 7. XANTHENE DYES AND PIGMENTS

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A preliminary study of the manufacture of Xanthene dyes was conducted to determine if process waste streams might contain hazardous material. The study first identifies the dyes and pigments that belong to this segment of the industry, the amounts produced and the known U.S. producers.

The chemistry of these dyes and pigments is discussed as well as the overall production process and waste treatment practices. Several waste streams that could contain hazardous material are identified and three companies that produce representative dyes and pigments are recommended for a sampling program to confirm the composition and amounts of these waste streams.

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report is one of a series of preliminary studies of segments of the dye and pigment manufacturing industry conducted for the Organic and Inorganic Chemicals and Products Branch of the Industrial Pollution Control Division. The objective of these studies was to determine if process waste streams might contain hazardous material and to recommend sites where a sampling program could be used to confirm the nature of any hazards that were identified.

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ABSTRACT

A preliminary study of the manufacture of Xanthene dyes was conducted to determine if process waste streams might contain hazardous material. The study first identifies the dyes and pigments that belong to this segment of the industry, the amounts produced and the known U.S. producers.

The chemistry of these dyes and pigments is discussed as well as the overall production process and waste treatment practices. Several waste streams that could contain hazardous material are identified and three companies that produce representative dyes and pigments are recommended for a sampling program to confirm the composition and amounts of these waste streams.

This report is submitted in fulfillment of contract No. 68-03-2944 by SRI International under the sponsorship of the U.S. Environmental Protection agency. The report covers the period December 1981 to August 1982, and work was completed as of July 31, 1983.

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SECTION 1

INTRODUCTION

The Resource Conservation and Recovery Act (RCRA) requires that hazardous solid wastes produced by manufacturing operations be identified and disposed in a manner that limits the release of hazardous materials to the environment. To date, many specific waste streams from manufacturing processes are listed in regulations as being hazardous because of their chemical composition. The objective of this study is to determine if wastes produced by the manufacture of dyes and pigments in the United States require listing as hazardous materials. An analysis of both the chemistry and the physical processing involved in dye and pigment manufacturing is used to identify all wastes that may contain significant chemical hazards. An analysis of the industry is used to determine specific manufacturers where the candidate wastes may be produced. This information allows contractors of the U.S. Environmental Protection Agency to design a sampling and analysis program to confirm or disprove the presence of hazardous materials in the candidate wastes and thereby develop a basis for listing dye and pigment manufacturing wastes under RCRA. This report deals with the wastes produced from the manufacture of xanthene dyes and pigments.

The xanthene dyes and pigments are characterized by pure, brilliant hues, by fluorescence, and by a range of colors from yellow to violet. In 1972, production of 530 metric tons for all xanthene dyes was reported to the U.S. Tariff Commission (1974). This represented 0.4% of the total reported U.S. dye production of 120,000 metric tons for that year. The xanthene dyes and pigments represented the ninth largest structural class of dyes based on U.S. production volume. Data on U.S. production by structural class have not been reported since 1972, so it is not possible to determine from public sources whether the relative importance or total production of xanthene dyes and pigments has changed.

The Colour Index (The Society of Dyers and Colourists, 1980) lists only 68 xanthene dyes, in contrast to more than 1000 entries for the largest class, the azo dyes. Although the xanthenes constitute a relatively small class, they have a wide variety of applications. In the textile field they are used for dyeing wool and silk directly and for dyeing cotton on a tannin mordant. Nontextile uses include the dyeing of wood, paper, and leather; the coloring of foods, drugs, and cosmetics; biological staining; and various applications in the printing industry. Xanthene lakes are used in paint, varnish, and printing applications.

Table 1 gives 1979 U.S. production data for the 27 commercially significant xanthene dyes and pigments--dyes produced at greater than 2.3 metric tons and pigments produced at greater than 0.5 metric tons. Production data are for the commercial product, which may include solvents, diluents, and impurities in addition to the specific dye chemical of interest; concentration of the organic dye in the commercial product may vary from 10% to 100%. No information was reported to the U.S. Tariff Commission concerning the concentration of the dye in the commercial product. Table 1 is arranged according to the Colour Index (C.I.) number (Colour Index, the Society of Dyers and Colourists, 1980). The 1979 U.S. production levels were taken from the Organic Dyes and Pigments Data Base prepared by SRI International (Swett et al., 1983).

For 18 dyes and 3 pigments the production is shown only as an amount greater than a minimum number. These are dyes and pigments produced by fewer than three manufacturers or by three or more where one or two dominate the market. Public sources do not list specific production amounts in these cases in order to protect trade secrets. Production of these 21 dyes and pigments could be substantial. The remaining six dyes and pigments listed in Table 1 have a known 1979 U.S. commercial production volume, and each of these dyes is produced by at least four manufacturers. These dyes and pigments are listed in Table 2, arranged according to their production volume. These six dyes represent a combined 1979 U.S. commercial production of 660 metric tons. The 1979 production of these six dyes and pigments alone account for more than the 1972 reported xanthene class production. Three of the dyes and pigments with reported production figures dominate the xanthene class: Food, Drug, and Cosmetic (FD&C) Red 3, Pigment Red 81 PMA, and Pigment Violet 1 PMA.

The Colour Index includes structures for all the dyes and pigments in Table 1 except Solvent Yellow 43. BIOS (1945) recipes, which describe process chemistry in detail, were found for 14 dyes (i.e., those represented by C.I. Numbers 45100 through 45170:2 and 45430 shown in Table 1).

In the following sections of this report the process chemistry of the xanthene dyes and pigments and sources of wastes during dye and pigment manufacture are discussed in detail.

Table 1

XANTHENE DYES AND PIGMENTS INCLUDED IN THIS STUDY

C.I. No.	C.I. Name[a]	1979 U.S. Commercial Production (metric tons/yr)
45100	Acid Red 52	> 2.3
45160	Basic Red 1	> 4.5
45160:1	Pigment Red 81, PMA[b]	205.0
45160:1	Pigment Red 81, PTA[b]	24.9
45160:2	Pigment Red 169	> 0.5
45170	Basic Violet 10	> 6.8
45170	Drug and Cosmetic Red 19	9.1
45170:1	Solvent Red 49	> 4.5
45170:1	Drug and Cosmetic Red 37	> 2.3
45170:2	Pigment Violet 1, fugitive[c]	> 0.9
45170:2	Pigment Violet 1, PMA[b]	147.0
45170:2	Pigment Violet 1, PTA[b]	20.4
45350	Acid Yellow 73	> 2.3
45350	Drug and Cosmetic Yellow 8	> 4.5
45350:1	Solvent Yellow 94	> 2.3
45350:1	Drug and Cosmetic Yellow 7	> 2.3
45370:1	Drug and Cosmetic Orange 5	> 4.5
45380	Acid Red 87	> 2.3
45380	Drug and Cosmetic Red 22	> 4.5
45380:1	Pigment Red 90	> 1.4
45380:2	Solvent Red 43	> 2.3
45380:2	Drug and Cosmetic Red 21	> 6.8
45410	Drug and Cosmetic Red 28	> 2.3
45410:1	Drug and Cosmetic Red 27	> 6.8
45425:1	Drug and Cosmetic Orange 10	> 6.8
45430	Acid Red 51	> 2.3

Table 1 (Concluded)

C.I. No.	C.I. Name[a]	1979 U.S. Commercial Production (metric tons/yr)
45430	Food, Drug, and Cosmetic Red 3	254.5
—	Solvent Yellow 43	> 2.3

[a]Many of the xanthene dyes are produced at a quality that allows usage in the drug and cosmetic and food industry. Dyes being manufactured for this purpose are listed by their Drug and Cosmetic name or their Food, Drug, and Cosmetic name. They are listed with their corresponding Colour Index number.

[b]The permanent basic dye pigments are produced by precipitation with complex inorganic heteropoly acids: phosphotungstic acid (PTA) and phosphomolybdic acid (PMA).

[c]The fugitive or nonpermanent pigments based on cationic dyes are usually precipitated with tannic acid or tartar emetic (antimony potassium tartrate). or with synthetic organic precipitants. Sometimes clay, fatty acids, or resin soaps are used as precipitants.

Table 2

XANTHENE DYES AND PIGMENTS OF KNOWN
1979 U.S. COMMERCIAL PRODUCTION

C.I. No.	C.I. Name[a]	1979 U.S. Commercial Production (metric tons/yr)
45430	Food, Drug, and Cosmetic Red 3	254.5
45160:1	Pigment Red 81, PMA[b]	205.0
45170:2	Pigment Violet 1, PMA[b]	147.0
45160:1	Pigment Red 81, PTA[b]	24.9
45170:2	Pigment Violet 1, PTA[b]	20.4
45170	Drug and Cosmetic Red 19	9.1

[a] Many of the xanthene dyes are produced at a quality that allows usage in the drug and cosmetic and food industry. Dyes being manufactured for this purpose are listed by their Drug and Cosmetic name or their Food, Drug, and Cosmetic name. They are listed with their corresponding Colour Index number.

[b] The permanent basic dye pigments are produced by precipitation with complex inorganic heteropoly acids: phosphotungstic acid (PTA), and phosphomolybdic acid (PMA).

SECTION 2

SUMMARY AND CONCLUSIONS

In this preliminary study of xanthene dyes and pigments, several waste streams were identified that might contain hazardous materials:

- Discarded shipping containers. These would contain dye and pigment intermediates.
- Process wastewater that may contain the mother liquor from filtering operations. This is probably the major source of discharge of organic chemicals from most plants.
- Wastewater treatment solids. The evidence indicates that the solids will be contaminated with low levels of all of the dye and pigment intermediates as well as the dyes and pigments themselves and some reaction by-products.

The three largest volume xanthene dyes each have phthalic anhydride as one intermediate. Because this chemical is used in excess and complete recovery of it may not be accomplished (BIOS, 1945), phthalic anhydride may dominate the organic fraction in wastewater from the production of xanthene dyes and pigments.

The information on the producers of dyes and pigments contained in Section 5 (Tables 6 and 7) along with the production volume information in Table 2 was analyzed to choose a few representative producers where a sampling program might be conducted to determine the composition of the waste emissions. The following companies are recommended:

Max Marx Color and Chemical Co.
Sun Chemical Corp.
Sterling Drug Inc., Hilton Davis Chemical Co. Division

These producers were selected by picking those which produce at least five xanthene dyes or pigments (Table 7), and at least one of those dyes was one of the top three in production volume (Table 2).

The three producers that are recommended for a sampling program should yield samples from facilities using different manufacturing and waste treatment practices. Since there is overlap in the actual dyes they produce, the three-producer sampling program increases the chances of identifying material in the waste streams from manufacturing the same dye or pigment that may be sensitive to plant practices.

SECTION 3

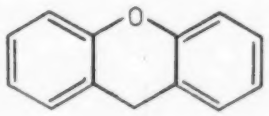
PROCESS CHEMISTRY

INTRODUCTION

A discussion of the production of xanthene dyes and pigments is necessary to identify the emission sources and wastes that might be hazardous. This section focuses on the chemistry of the dye and pigment synthesis with special attention given to the starting materials, intermediates, reaction conditions, and potential by-products.

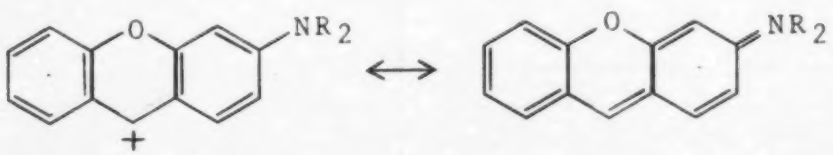
In general, xanthene dyes are cationic (basic) dyes. The class, however, includes acid and spirit-soluble dyes and mordant colors and lakes. The acid dyes, which contain carboxyl and phenolic hydroxyl groups or the sulfonic group, are fluoresceins. Spirit-soluble dyes are obtained by esterification of the carboxyl group, and mordant dyes can be made by introducing o-dihydroxybenzene or salicylic acid moieties. Lakes can be obtained by precipitation of hydroxyl- or carboxyl-containing dyes with salts of metals such as lead or aluminum.

The dyes of the xanthene class (C.I. 45000-45999) are based on xanthene, the chromophore being the xanthylium nucleus and the usual auxochromes being amino or hydroxy groups meta to the oxygen atom.



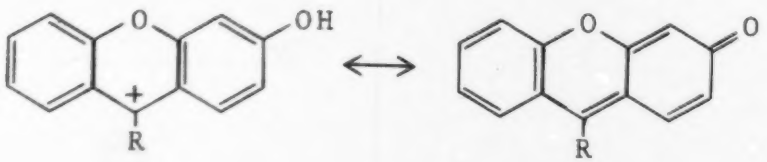
Xanthene

The chromophore of the aminoxanthene dyes (the resonance-hybrid) is shown below where R = H, alkyl, or aryl.



Aminoxanthene Chromophore

The hydroxyxanthenes can be stabilized by the loss of a proton, forming an uncharged system in which the chromophore is the quinoid structure.



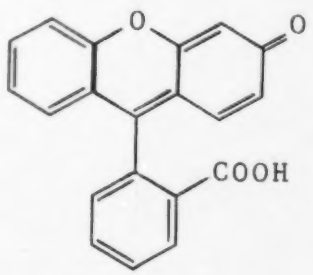
Hydroxyxanthene Quinoid Structure

The xanthene dyes are not obtained from xanthene itself, but by reacting together suitably chosen simple intermediates. In general, the condensation reaction to make xanthene dyes and pigments is performed with 100% stoichiometric excess of the acid component (such as phthalic anhydride), which is later recovered.

The purified dye products, Drug and Cosmetic (D&C) and Food, Drug, and Cosmetic (FD&C), are made by redissolving the dye of interest in water followed by filtration and reprecipitation (BIOS, 1945).

PREPARATION OF ACID DYES

Baeyer (1871) first synthesized the acid dye fluorescein (Solvent Yellow 94, C.I. 45350:1) from phthalic anhydride and resorcinol.



Fluorescein (C.I. 45350:1)

Fluorescein is no longer used as a textile dye, but, because of its strong fluorescence, it is used as a water-flow tracer.

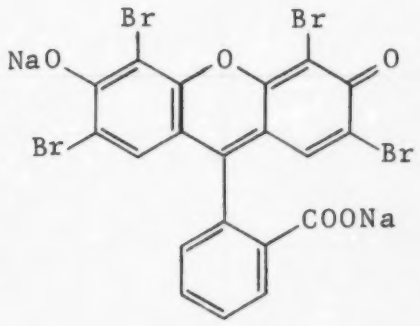
The disodium and dipotassium salts of fluorescein are known as uranine (Acid Yellow 73 C.I. 45350). The other forms of fluorescein are Drug and Cosmetic (D&C) Yellow 8 (C.I. 45350) and D&C Yellow 7 (C.I. 45350:1). These are the purified forms of Acid Yellow 73 and Solvent Yellow 94, respectively.

Several important dyes are obtained by halogenation of fluorescein. The substitution of bromine or iodine for hydrogen in a dye molecule often has an important and desirable effect on the properties of a dye or the pigment (such as deeper shade and increased reactivity to the fiber).

Fluorescein is prepared by condensing two moles of resorcinol (m-dihydroxybenzene) with one mole of phthalic anhydride in the presence of a catalyst such as zinc chloride (Robitschek, 1943). The dye synthesis takes about 20 hours (BIOS, 1945). Steadman et al. (1977) state that ferric chloride may be used as a replacement for zinc chloride.

Halogenations are generally performed at temperatures in the range of 40 to 55°C in a solvent medium such as sodium hydroxide in water or ethanol in water. Only half of the halogen used appears in the product. The remaining amount is converted to the hydrogen halide or sodium halide and the by-product halide is recovered (BIOS, 1945). Recovery of the solvent ethanol is also practiced.

The disodium salt of 2,4,5,7-tetrabromofluorescein is commonly known as Eosine (Acid Red 87, C.I. 45380).

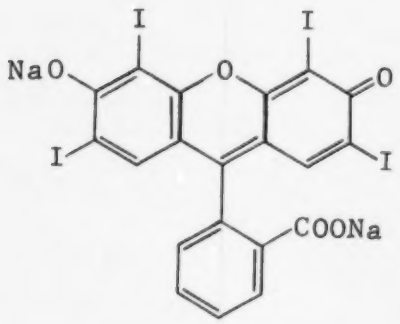


Eosine (C.I. 45380)

It may be obtained by boiling fluorescein, in acidic aqueous alcohol, with bromine and sodium chlorate, followed by conversion to the sodium salt. Eosine has been used in the production of red lakes and toners that are used extensively in printing inks. The lead lake of eosine, Pigment Red 90 (C.I. 45380:1), is prepared by precipitation of eosine with a soluble lead salt.

The other forms of eosine consist of the free acid (Solvent Red 43, C.I. 45380:2 and D&C Red 21 C.I. 45380:2) and D&C Red 22 (C.I. 45380).

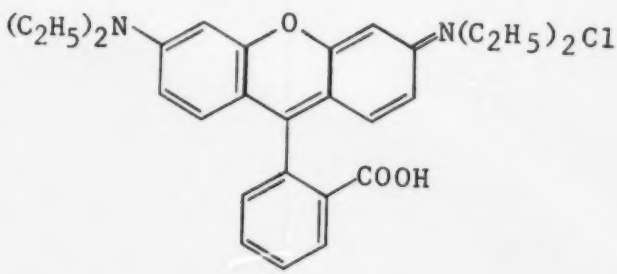
Erythrosine, Acid Red 51 (C.I. 45430), is made by tetraiodination of fluorescein using iodine and potassium iodate. This dye has the largest reported 1979 production volume of the xanthene dyes and pigments included in this study.



Erythrosine (C.I. 45430)

PREPARATION OF AMINO-SUBSTITUTED XANTHENE DYES

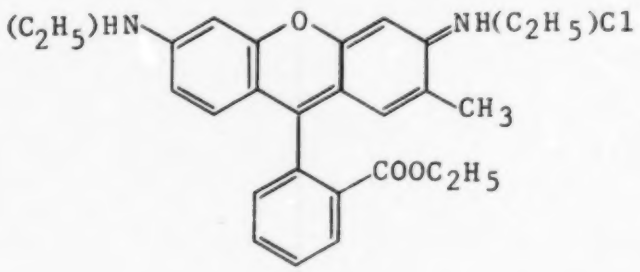
The most important amino-substituted xanthene dyes, the rhodamines, are basic dyes, although acid rhodamines may be obtained by introducing the sulfonic acid group. The free base, Rhodamine B base (Solvent Red 49, C.I. 45170:1), and Rhodamine B (Basic Violet 10, C.I. 45170) are prepared commercially by the condensation of two moles of m-diethylaminophenol with phthalic anhydride.



Rhodamine B (C.I. 45170)

The aminophenol is added gradually to the phthalic anhydride at less than 180°C over a 3-hour period. Cyclization of the intermediate product is accomplished with 78% sulfuric acid at 180°C in 3 hours. For Rhodamine B the reaction mixture is dumped into water (drowned), and the finished dye is salted out of the drowned reaction mixture with sodium chloride (Steadman, et al., 1977). An alternative synthesis route is via the action of diethylamine on 3',6'-dichlorofluoran under pressure.

Rhodamine 6G (Basic Red 1, C.I. 45160) is an esterified rhodamine. It is prepared by condensing 3-ethylamino-p-cresol with phthalic anhydride and esterifying the product with ethyl chloride in 94% ethanol at 120°C and 7 to 8 atmospheres for several hours. Magnesium oxide is used as a catalyst. Esterification improves the solubility of the product in alcohol solvents.



Rhodamine 6G

PREPARATION OF XANTHENE PIGMENTS

Xanthene pigments may be manufactured from the cationic dyes by precipation, using either insoluble tannates, clay, or tartar emetic (antimony potassium tartrate) substrates. However, the uses of these products are restricted by their low light fastness, and they are known as fugitive pigments. Only one commercially significant xanthene pigment is reported to be fugitive (Pigment Violet, 1 fugitive, C.I. 45170:2).

It was discovered that improved light fastness could be obtained with complex acid precipitants, such as phosphotungstic and phosphomolybdic acids (PTA and PMA, respectively), or their salts (Allen, 1971; Allen, 1955). As a result, the second largest volume xanthene dye or pigment included in this study is Pigment Red 81, PMA (C.I. 45160:1), and the third largest is Pigment Violet 1, PMA (C.I. 45170:2).

SECTION 4

ORGANIC AND INORGANIC INTERMEDIATES AND REAGENTS USED IN XANTHENE DYE AND PIGMENT PRODUCTION

A list of organic and inorganic intermediates and reagents used to produce the xanthene dyes with known composition in the United States was compiled from information in the Colour Index (The Society of Dyers and Colourists, 1980), BIOS Reports No. 959 and 1443 (1945), and Steadman, et al. (1977). Table 3 lists the organic and inorganic intermediates and reagents used in the production of the 26 dyes and pigments for which process information was available. Table 3 also identifies those substances which, if present in solid wastes, are subject to regulation as hazardous wastes under RCRA (Federal Register, 1980). These substances are identified by their hazard code.

Table 3

ORGANIC AND INORGANIC INTERMEDIATES AND REAGENTS USED TO PRODUCE XANTHENE DYES AND PIGMENTS WITH KNOWN COMPOSITION

Organic Intermediate or Reagent	Hazardous Waste Listing[a]
m-Diethylaminophenol	
m-Dihydroxybenzene (Resorcinol)	T
Ethanol	
Ethyl chloride	
3-Ethylamino-p-cresol	T
4-Formyl-m-benzenedisulfonic acid	
Phthalic anhydride	T
o-Dichlorobenzene	T
Tetrachlorophthalic anhydride	
Inorganic Intermediate or Reagent	
Ammonia	
Bromine	
Copper ferrocyanide	H
Ferric chloride	
Hydrochloric acid	
Iodine	
Magnesium oxide	
Lead salts	T
Nitric acid	
Sodium hydroxide	
Sulfuric acid	
Zinc chloride	
Phosphotungstic acid	
Phosphomolybdic acid	
Antimony potassium tartrate	T

[a]Hazard codes from the Federal Register, (1980) indicate the basis for EPA listing the material hazardous: Acute Hazardous (H) and Toxic (T).

SECTION 5

SOURCES OF WASTE DISCHARGES DURING DYE AND PIGMENT MANUFACTURING

The wide range of dye and pigment production processes and the specific plant characteristics and process control capabilities make estimation of material losses during dye manufacture a difficult task. In general, the most significant material losses are intermediates that do not react and by-products such as incomplete dye or pigment molecules. The intermediates and by-products from the dye manufacture are present either in the product or in the solid waste streams regulated under RCRA--wastewater, solid residues, or the vapor and dust emissions. The material in the wastewater is discharged in the plant effluent, and some is discharged on wastewater treatment solids.

OVERVIEW OF DYE AND PIGMENT PRODUCTION PROCESSES

Figure 1 illustrates the dye and pigment manufacturing process and shows where the losses of materials occur. The dye manufacturing equipment required to produce xanthene dyes and pigments consists of stationary reaction kettles (glass-lined, with heavy-duty agitators), rotary bakers (equipped with balls or rods for mixing), and standard filter presses, grinders, dryers, and blenders. (Steadman, et al., 1977; BIOS, 1945).

The dyes or pigments are produced in batches, and the plants typically contain several reactor trains. Complex dyes and pigments may require use of several reactor trains. Production of colors is usually rotated by set schedules from light- to dark-colored dyes to minimize the impact of dye carry-over from multiple use of the equipment.

The sources of wastes from dye manufacture identified in Figure 1 are summarized below:

- Material handling--Air emissions from raw material dusting and volatilization, solid residues on shipping containers, and process wastewaters from equipment washdown.
- Dye synthesis--Air emissions from the volatilization of unreacted intermediates and by-products from reaction vessels, solid residues from distillation residues and spills, and process wastewaters from equipment washdown.
- Product and intermediate filtration--Air emissions from unreacted intermediate and by-product volatilization during material handling, solid residues from spills, and process wastewater from equipment

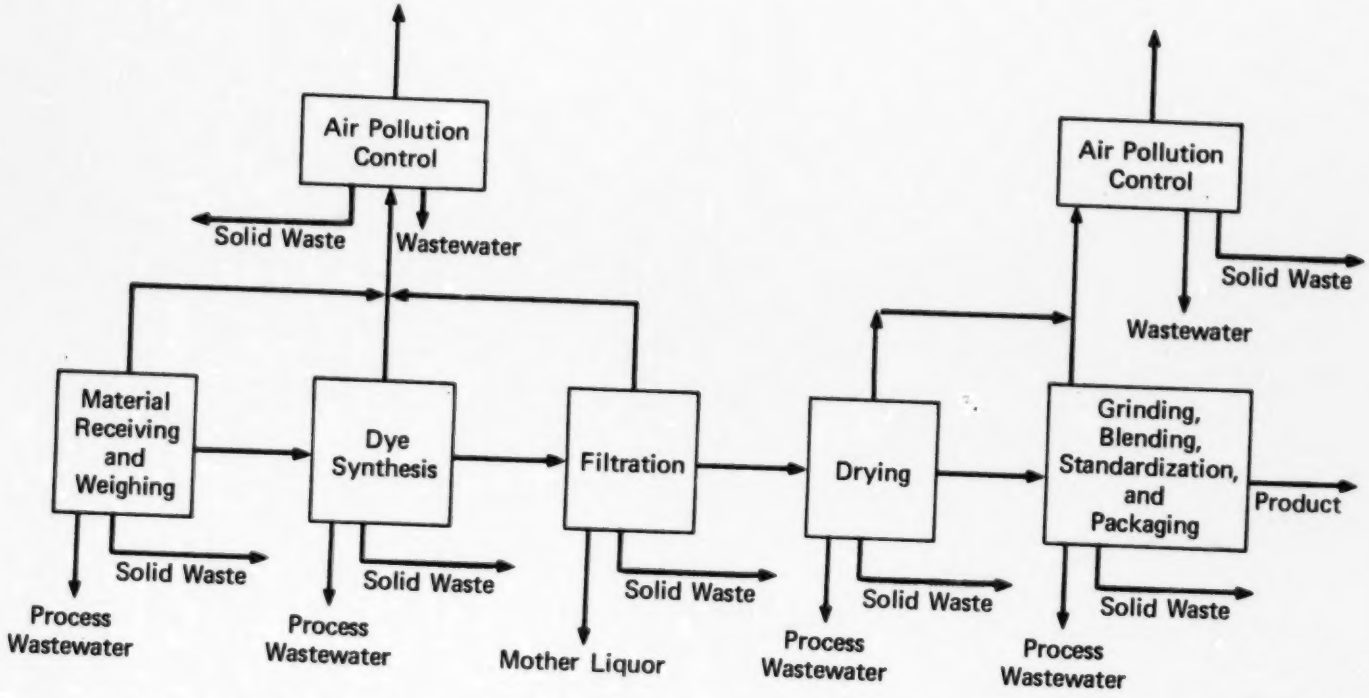


FIGURE 1 PRODUCTION OPERATIONS THAT ARE SOURCES OF WASTE EMISSIONS IN DYE AND PIGMENT MANUFACTURE

washdown. A significant source of process wastewater is the mother liquor following dye or pigment precipitation and filtration.

- Drying--Air emissions from volatilization of by-products, solvents, and unreacted intermediates in the drying oven, and solid residues from spills and dusting of the product dye.
- Grinding, blending, standardization, and packaging--Solid residues from dusts produced by the grinding operations that may be in the air streams from vent systems designed to prevent the material from entering the workplace environment or in the solid residue from spills.
- Air pollution control--Solid residues from baghouses or scrubbers collecting fine dust and process wastewater from scrubbers.

MATERIAL IN THE WASTE STREAMS FROM XANTHENE DYE PRODUCTION

Previous studies (Lapp et al., 1979; Bomberger and Boughton, 1983) have demonstrated that the major potential source of emissions is the process wastewater, primarily because it contains the mother liquor.

On the basis of the chemistry discussed in Section 3, these mother liquors, obtained from filtering the dyes, will probably contain solvents, unreacted intermediates, reaction by-products, unprecipitated dye or pigments, and salt. They may also contain mineral acids, such as sulfuric and hydrochloric acid.

Steadman, et al. (1977) report that the waste streams from xanthene dye production are mainly brines contaminated with small amounts of organic chemicals, which are highly colored.

Phthalic anhydride is used in excess and is recovered by acid precipitation and filtration, distillation, or by extraction of the mother liquor with o-dichlorobenzene. Phthalic anhydride losses reported in the BIOS reports are 12 kg per 100 kg of dye for C.I. 45160 group dyes and pigments and 13 kg per 100 kg of dye for the C.I. 45170 group. Some of this lost phthalic anhydride will probably be in the mother liquor that is discharged to the wastewater treatment system. Ethanol (for esterification) is also added in excess and a majority is recovered. Twenty kg of ethanol per 100 kg of dye is reported lost from the synthesis of the C.I. 45160 group dyes and pigments and 38 kg per 100 kg of dye from the C.I. 45430 group.

The solvent recovery operations to recover phthalic anhydride generate a hazardous waste stream because the spent solvent o-dichlorobenzene is considered a hazardous material (Federal Register, 1980).

Vapors, such as those of iodine, bromine, ethanol, and sulfur dioxide, may be released during synthesis and filtration operations of certain xanthene dyes. Sulfur dioxide, ethanol, and iodine vapors are reported to be released from Acid Red 51 (C.I. 45430) production (BIOS, 1945). Iodine is also

recovered from the mother liquor from the synthesis of Acid Red 51. The loss of iodine from this process is about 3 kg per 100 kg of unstandardized dye. Suspended hydrous iron oxide may also be present because of the use of ferric chloride as a condensation agent (BIOS, 1945).

Eight of the xanthene dyes included in Table 1 are listed in Table 4, which shows their reported dye purity (unstandardized) and dye yields (BIOS, 1945). The yields of each dye (that is reported in the BIOS reports) gives an indication of how much by-product or unreacted intermediate remains in the reaction liquor. These unreacted intermediates or by-products may remain in the mother liquor or precipitate with the dye product.

The high dye concentration in the precipitated product (in some cases more than 99 wt% as dye) shows that most of the xanthene dyes are relatively pure products following precipitation and filtration. It is not possible to determine what the residual material is.

Table 5 lists the xanthene dyes and pigments produced in 1979 for which the chemical composition information was available. The wastes estimated to be produced by the manufacture of these materials are also shown in the table. Table 5 does not identify process chemistry by-products that are likely to be present, for example, isomers of required intermediates and the reaction product of these with the other intermediates and reagents used in the process. The by-products were not within the scope of this study because little useful information regarding the amount or nature of these by-products was found.

The producers of the xanthene dyes are indicated by a letter code in Table 5. Table 6 gives the full names of the producers associated with the letter codes in Table 5. Table 7 lists all the producers of xanthene dyes and pigments and the dyes they manufacture. The identity and corporate ownership of the producers is based on 1979 information. Since then, several dye production facilities or dye lines were sold. Sales that were announced in trade journals are shown as footnotes to Tables 6 and 7. A systematic search was not made to verify that all such sales have been listed, so the tables may not be complete.

Table 4

EXAMPLES OF PRODUCT PURITY AND YIELD FOR THE XANTHENE DYES

C.I. No.	C.I. Name	Dye Concentration (wt%)	Percent of Theoretical Yield
45100	Acid Red 52	95+	--
45160	Basic Red 1	96	--
45170	Basic Violet 10	99	96
45350	Acid Yellow 73	99+	--
45370:1	Drug and Cosmetic Orange 5	73	--
45380	Acid Red 87	99+	--
45425:1	Solvent Red 73	99+	--
45430	Acid Red 51	88	88

Source: Bios (1945).

Table 5

ORGANIC AND INORGANIC MATERIALS THAT MAY APPEAR IN THE WASTE STREAMS FROM THE PRODUCTION OF XANTHENE DYES AND PIGMENTS
(Common inorganics such as sodium chloride and hydrochloric or sulfuric acid, sodium hydroxide, and ammonia are not included)

1979 U.S. Commercial Producers	C.I. No.	C.I. Name	1979 U.S. Commercial Production (metric tons/yr)	Materials Released to the Environment
CK	45100	Acid Red 52	>2.3	Acid Red 52 4-Formyl-m-benzenesulfonic acid Ferric chloride
BAS DUP	45160	Basic Red 1	>4.5	Basic Red 1 3-Ethylamino-p-cresol Phthalic anhydride Ethanol Ethyl chloride Magnesium oxide
BAS,MGR CGY,MRX DUP,SNA	45160:1	Pigment Red 81, PMA[a]	205.0	Pigment Red 81 3-Ethylamino-p-cresol Phthalic anhydride Ethyl chloride Magnesium oxide PMA
BAS,MGR CGY,MRX NCW,UHL KON	45160:1	Pigment Red 81, PTA[a]	24.9	Pigment Red 81 3-Ethylamino-p-cresol Phthalic anhydride Ethanol Ethyl chloride Magnesium oxide PTA
HST	45160:2	Pigment Red 169	>0.5	Pigment Red 169 3-Ethylamino-p-cresol Phthalic anhydride Ethanol Ethyl Chloride Copper ferrocyanide
ACY BAS DUP	45170	Basic Violet 10	>6.8	Basic Violet 10 m-Diethylaminophenol Phthalic anhydride Alumina hydrate

Table 5 (Continued)

1979 U.S. Commercial Producers	C.I. No.	C.I. Name	1979 U.S. Commercial Production (metric tons/yr)	Materials Released to the Environment
BCC, SNA KON, TMS SDH	45170	D&C Red 19	9.1	D&C Red 19 m-Diethylaminophenol Phthalic anhydride Aluminum hydrate
ACY DUP	45170:1	Solvent Red 49	>4.5	Solvent Red 49 m-Diethylaminophenol Phthalic anhydride Aluminum hydrate
BCC	45170:1	D&C Red 37[b]	>2.3	D&C Red 37 m-Diethylaminophenol Phthalic anhydride Aluminum hydrate
CGY MGR MRX SNA	45170:2	Pigment Violet 1, PTA[a]	20.4	Pigment Violet 1 PTA m-Diethylaminophenol Phthalic anhydride Aluminum hydrate PTA
CGY MGR MRX SNA UHL	45170:2	Pigment Violet 1 PMA[a]	147.0	Pigment Violet 1 m-Diethylaminophenol Phthalic anhydride Alumina hydrate PMA
KCW UHL	45170:2	Pigment Violet 1, Fugitive[c]	>0.9	Pigment Violet 1 m-Diethylaminophenol Phthalic anhydride Aluminum hydrate clay or tartar emetic
SDH	45350	Acid Yellow 73	>2.3	Acid Yellow 73 m-Dihydroxybenzene Phthalic anhydride Zinc chloride
SDH TMS	45350	D&C Yellow 8	>4.5	D&C Yellow 8 m-Dihydroxybenzene Phthalic anhydride Zinc chloride

Table 5 (Continued)

1979 U.S. Commercial Producers	C.I. No.	C.I. Name	1979 U.S. Commercial Production (metric tons/yr)	Materials Released to the Environment
SDH	45350:1	Solvent Yellow 94[d]	>2.3	Solvent Yellow 94 m-Dihydroxybenzene Phthalic anhydride Zinc chloride
BCC	45350:1	D&C Yellow 7[d]	>2.3	D&C Yellow 7 m-Dihydroxybenzene Phthalic anhydride Zinc chloride
SDH SNA	45370:1	D&C Orange 5	>4.5	D&C Orange 5 m-Dihydroxybenzene Bromine Nitric acid Zinc chloride
SDH	45380	Acid Red 87	>2.3	Acid Red 87 m-Dihydroxybenzene Phthalic anhydride Ethanol Bromine Zinc chloride
BCC SDH	45380	D&C Red 22	>4.5	D&C Red 22 m-Dihydroxybenzene Phthalic anhydride Ethanol Bromine Zinc chloride
AMS BOR	45380:1	Pigment Red 90[e]	>1.4	Pigment Red 90 m-Dihydroxybenzene Bromine Lead salt Zinc chloride
SDH	45380:2	Solvent Red 43[f]	>2.3	Solvent Red 43 m-Dihydroxybenzene Phthalic anhydride Ethanol Bromine Zinc chloride

Table 5 (Concluded)

1979 U.S. Commercial Producers	C.I. No.	C.I. Name	1979 U.S. Commercial Production (metric tons/yr)	Materials Released to the Environment
MRX SDH SNA	45380:2	D&C Red 21[f]	>6.8	D&C Red 21 M-Dihydroxybenzene Phthalic anhydride Ethanol Bromine Zinc chloride
SDH	45410	D&C Red 28	>2.3	D&C Red 28 m-Dihydroxybenzene Tetrachlorophthalic anhydride
MRX SDH TMS	45410:1	D&C Red 27[g]	>6.8	D&C Red 27 m-Dihydroxybenzene Tetrachlorophthalic anhydride Bromine
BDO	45430	Acid Red 51	>2.3	Acid Red 51 m-Dihydroxybenzene Phthalic anhydride Ethanol Iodine Zinc chloride
BDO CK KON SDH STG WJ	45430	FD&C Red 3	254.5	FD&C Red 3 m-Dihydroxybenzene Phthalic anhydride Ethanol Iodine Zinc cloride
DGO	-	Solvent Yellow 43	>2.3	Solvent Yellow 43 Unknown

[a]The permanent basic dye pigments are produced by precipitation with complex inorganic heteropoly acids: phosphotungstic acid (PTA) and phosphomolybdic acid (PMA).

[b]Solvent Red 49 and D&C Red 37 are the free base forms of Basic Violet 10 (the chloride salt).

[c]The fugitive or nonpermanent pigments based on cationic dyes are usually produced by precipitation with tannic acid and tartar emetic (antimony potassium tartrate), or with synthetic organic precipitants. Sometimes clay, fatty acids, or resin soaps are used as precipitants.

[d]Solvent Yellow 94 and D&C Yellow 7 are the free acid forms of Acid Yellow 73 (the disodium salt).

[e]Pigment Red 90 is the lead salt of Acid Red 87 (the disodium salt).

[f]Solvent Red 43 and D&C Red 21 are the free acid forms of Acid Red 87 (the disodium salt).

[g]D&C Red 27 is the free acid form of D&C Red 28 (the disodium salt).

Table 6

DIRECTORY OF DYE AND ORGANIC
PIGMENT MANUFACTURERS, 1979

Names of manufacturers that reported production and/or sales of xanthene dyes and pigments to the U.S. International Trade Commission for 1979 are listed below in order of their identification codes as used in Table 5.

Code	Name of Company
Dye Manufacturers	
ACY	American Cyanamid Co.
BAS	BASF Wyandotte Corp., Pigments Div.
BCC	Buffalo Color Corp.
BDO	Benzenoid Organics, Inc.
CK	Crompton & Knowles Corp., Dyes & Chemical Div.
DGO	Day-Glo Color Corp.
DUP[a]	E.I. duPont de Nemours & Co., Inc.
KON	H. Kohnstamm & Co., Inc.
MRX	Max Marx Color & Chemical Co.
SDH	Sterling Drug, Inc., Hilton Davis Chemical Co. Div.
SNA	Sun Chemical Corp.
STG	Stange Co.
TMS	Sterling Drug, Inc., Thomasset Colors Div.
WJ	Warner-Jenkinsen Co.
Pigment Manufacturers	
AMS	Ridgway Color & Chemical
BAS	BASF Wyandotte Corp. & Pigments Div.
BOR	Borden, Inc., Printing Ink Div., Pigments Div.
CGY	Ciba-Geigy Corp.
DUP	E.I. duPont de Nemours & Co., Inc.
HST	American Hoechst Corp., Industrial Chemicals Div.
KCW	Keystone Color Works, Inc.
KON	H. Kohnstamm & Co., Inc.
MGR	Magruder Color Co., Inc.
MRX	Max Marx Color & Chemical Co.
SDH	Sterling Drug, Inc., Hilton Davis Chemical Co. Div.
SNA	Sun Chemical Corp.
UHL	Paul Uhlich & Co., Inc.

[a]In 1979 duPont sold its paper dye operations to Mobay Chemical Corp., and its textile dye operations to Ciba-Geigy Corp. and Crompton and Knowles Corp.

Table 7

1979 PRODUCERS OF XANTHENE
DYES AND PIGMENTS

C.I. No.	C. I. Name[a]
American Cyanamid Co.	
45170	Basic Violet 10
45170:1	Solvent Red 49
Ridgway Color & Chemical	
45380:1	Pigment Red 90
BASF Wyandotte Corp., Pigments Div.	
45160	Basic Red 1
45160:1	Pigment Red 81, PMA[b]
45160:1	Pigment Red 81, PTA[b]
45170	Basic Violet 10
Buffalo Color Corp.	
45170	Drug and Cosmetic Red 19
45170:1	Drug and Cosmetic Red 37
45350:1	Drug and Cosmetic Yellow 7
45380	Drug and Cosmetic Red 22
Benzenoid Organics, Inc.	
45430	Acid Red 51
45430	Food, Drug, and Cosmetic Red 3
Borden, Inc., Printing Ink Div., Pigments Div.	
45380:1	Pigment Red 90

C.I. No.	C.I. Name
Ciba-Geigy	
45160:1	Pigment Red 81, PMA[b]
45160:1	Pigment Red 81, PTA[b]
45170:2	Pigment Violet 1, PMA[b]
45170:2	Pigment Violet 1, PTA[b]
Crompton & Knowles Corp., Dyes & Chemical Div.	
45100	Acid Red 52
45430	Food, Drug, and Cosmetic Red 3
Day-Glo Color Corp.	
-	Solvent Yellow 43
E. I duPont de Nemours & Co., Inc.[c]	
45160	Basic Red 1
45160:1	Pigment Red 81, PMA[b]
45170	Basic Violet 10
45170:1	Solvent Red 49
American Hoechst Corp., Industrial Chemicals Div.	
45160:2	Pigment Red 169
Keystone Color Works, Inc.	
45160:1	Pigment Red 81, PTA[b]
45170:2	Pigment Violet 1, fugitive[d]

Table 7 (Continued)

C.I. No.	C.I. Name
H. Kohnstamm & Co., Inc.	
45160:1	Pigment Red 81, PMA[b]
45160:1	Pigment Red 81, PTA[b]
45170	Drug and Cosmetic Red 19
45430	Food, Drug, and Cosmetic Red 3
Magruder Color Co., Inc.	
45160:1	Pigment Red 81, PMA[b]
45160:1	Pigment Red 81, PTA[b]
45170:2	Pigment Violet 1, PMA[b]
45170:2	Pigment Violet 1, PTA[b]
Max Marx Color & Chemical Co.	
45160:1	Pigment Red 81, PMA[b]
45160:1	Pigment Red 81, PTA[b]
45170:2	Pigment Violet 1, PMA[b]
45170:2	Pigment Violet 1, PTA[b]
45380:2	Drug and Cosmetic Red 21
45410:1	Drug and Cosmetic Red 27
Sterling Drug, Inc., Hilton Davis Chemical Co. Div.	
45170	Drug and Cosmetic Red 19
45350	Acid Yellow 73
45350	Drug and Cosmetic Yellow 8
45350:1	Solvent Yellow 94
45370:1	Drug and Cosmetic Orange 5
45380	Acid Red 87

C.I. No.	C. I. Name
Sterling Durg, Inc. Hilton Davis Chemical Co. Div. (Cont)	
45380	Drug and Cosmetic Red 22
45380:1	Pigment Red 90
45380:2	Solvent Red 43
45380:2	Drug and Cosmetic Red 21
45410	Drug and Cosmetic Red 28
45410:1	Drug and Cosmetic Red 27
45430	Food, Drug, and Cosmetic Red 3
Sun Chemical Corp.	
45160:1	Pigment Red 81, PMA[b]
45170	Drug and Cosmetic Red 19
45170:2	Pigment Violet 1, PMA[b]
45170:2	Pigment Violet 1, PTA[b]
45370:1	Drug and Cosmetic Orange 5
45380:2	Drug and Cosmetic Red 21
Stange Co.	
45430	Food, Drug, and Cosmetic Red 3
Sterling Drug, Inc., Thomasset Colors Div.	
45170	Drug and Cosmetic Red 19
45350	Drug and Cosmetic Yellow 8
45410:1	Drug and Cosmetic Red 27

Table 7 (Concluded)

C.I. No.	C. I. Name
Paul Uhlich & Co., Inc.	
45160:1	Pigment Red 81, PMA[b]
45160:1	Pigment Red 81, PTA[b]
45170:2	Pigment Violet 1, fugitive[d]
45170:2	Pigment Violet 1, PMA[b]
Warner-Jenkinson Co.	
45430	Food, Drug, and Cosmetic Red 3

[a]Many of the xanthene dyes are produced at a quality which allows usage in the drug and cosmetic and food industry. Dyes being manufactured for this purpose are listed by their Drug and Cosmetic name or their Food, Drug, and Cosmetic name. They are listed with the corresponding Colour Index number.

[b]The permanent basic dye pigments are produced by precipitation with complex inorganic heteropoly acids: phosphotungstic acid (PTA) and phosphomolybdic acid (PMA).

[c]In 1979 DuPont sold its paper dye operations to Mobay Chemical Corp., and its textile dye operations to Ciba-Geigy Corp. and Crompton and Knowles Corp.

[d]The fugitive or nonpermanent pigments based on cationic dyes are usually precipitated with tannic acid or tartar emetic (antimony potassium tartrate), or with synthetic organic precipitants. Sometimes clay, fatty acids, or resin soaps are used as precipitants.

REFERENCES

Allen, E. R. 1955. Organic Pigments. Chapter 11 in: The Chemistry of Synthesis Dyes and Pigments, edited by H. A. Lubs, Reinhold Publishing Corp., New York.

Allen, R. L. M. 1971. Colour Chemistry. Appleton-Century-Crofts, New York.

Baeyer, A. 1871, Chem. Ber., 4, 555, 658.

BIOS (British Intelligence Objectives Subcommittee). 1945. The Development of New Dyes and Colour Application Processses in Germany and Italy During World War II. Reports No. 957 and 1443. H. M. Stationery Office, London.

Bomberger, D. C., and R. L. Boughton. 1983. Wastes from Manufacture of Dyes and Pigments (Benzidine and Its Congeners Subsector). U.S. Environmental Protection Agency, Office of Research and Development, Industrial Environmental Research Laboratory, Cincinnati, Ohio. Contract No. 68-03-2934.

Federal Register. 1980. Identification and Listing of Hazardous Waste. 45(98): 33119-33133 (May 19, 1980).

Lapp, T. W., T. L. Ferguson, H. Gadberry, F. Hoffmeister, F. Hopkins, and B. Thompson. 1979. A Preliminary Materials Balance for Dyes and Pigments from Benzidine and Three Benzidine Derivatives. Midwest Research Institute Draft Report for the U.S. Environmental Protection Agency, Office of Toxic Substances, Washington, D.C.

Robitschek, F. O., 1943. U.S. Dept. Comm. Office Tech. Serv. PB Rept 70135, Reel 18G, Frames 1125-1135.

The Society of Dyers and Colourists. 1980. Colour Index. Lund Humphries Printers, London, England, Volumes 103, Third Edition, 1971; Volume 6, Revised Third Edition, 1975; Additions and Amendments Numbers 18-36, October 1974-July 1980.

Steadman, T. R., E. W. Helper, T. Parsons, G. E. Wilkins, and N. R. Phillips. 1977. Industrial Process Profiles for Environmental Use: Chapter 7. Organic Dyes and Pigments Industry. U.S. NTIS PB 281479. EPA 600/2-77-023g. U.S. Environmental Protection Agency, Office of Research and Development, Industrial Environmental Research Laboratory, Cincinnati, Ohio.

Swett, L. A. Twhigg, and K. E. McCaleb. 1983. The Organic Dyes and Pigments Data Base. U.S. Environmental Protection Agency, Office of Research and Development, Industrial Environmental Research Laboratory, Cincinnati, Ohio. EPA Contract No. 68-03-2944.

U.S. Tariff Commission (USTC). 1974. Synthetic Organic Chemicals, U.S. Production and Sales, 1972. TC Publication 681, U.S. Government Printing Office, Washington, D.C.

U.S. International Trade Commission (USITC). 1980. Synthetic Chemicals, U..S. Production and Sales, 1979. TC Publication 1099, U.S. Government Printing Office, Washington, D.C.